Cathode Contact Material Development

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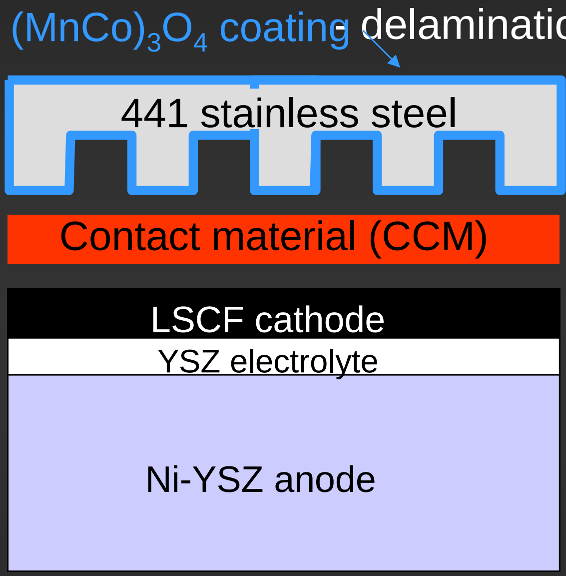
Problem Statement

Well-bonded CCM is desirable, but challenging

- Loose powder CCM is acceptable if stack experiences uniform compression

BUT: cross-cell thermal gradients, warping of components, etc causes local variation delamination and loss of electrical contact



Bonding at 1000°C or less to avoid oxidation of steel

This is a low sintering/bonding temperature!!
- poor bonding
- incomplete sintering = reduced conductivity

Can we find a material reactive enough to bond at <1000°C but stable at 800°C operation?

Our work suggests that CCM composites is a valid concept to improve bonding without sacrifice electrical performance

Our Approach

Approach 1:
Select CCMs from cathode materials set

- Assess conductivity, sintering, CTE, reaction with LSCF and MCO
- Down-select most promising candidates and do ASR testing

Novel CCM-Composites Idea

Approach 2: Glass- CCM composite
Approach 3: Inorganic binders

In-situ assessment

- Electrochemical performance
- High-temperature delamination testing

Approach 1: Selection of pure conventional CCM

Candidate Materials

CCM requirements:
- good bonding
- high electronic conductivity
- good CTE match
- chemical compatibility with LSCF and $(MnCo)_3O_4$

Approach:
Select candidates from cathode literature
- high conductivity
- low sintering temperature

La0.6Sr0.4Co0.8Fe0.2	LSCF
La0.8Sr0.2Cu0.9Fe0.1O2.5	LSCuF
La0.7Sr0.3CoO3	LSC
Sm0.5Sr0.5CoO3	SSC
SmBa0.5Sr0.5Co2O5	SBSC
GdSrCo2O5	GSC
La0.65Sr0.30MnO3	LSM
LaBaCo2O5	LBC
YBaCo2O5	YBC
Nd1.8Ce0.2CuO4	NCC
La0.8Sr0.2Co0.3Mn0.1Fe0.6O3	LSCMF
La0.98Ni0.6Fe0.4O3	LNF
La1.2Sr0.8NiO4	LSN
La0.7Sr0.3FeO3	LSF
La2Ni0.6Cu0.4O4	LNC

LSM, LNF, SSC, LSCF purchased from Praxair

All others synthesized by GNP

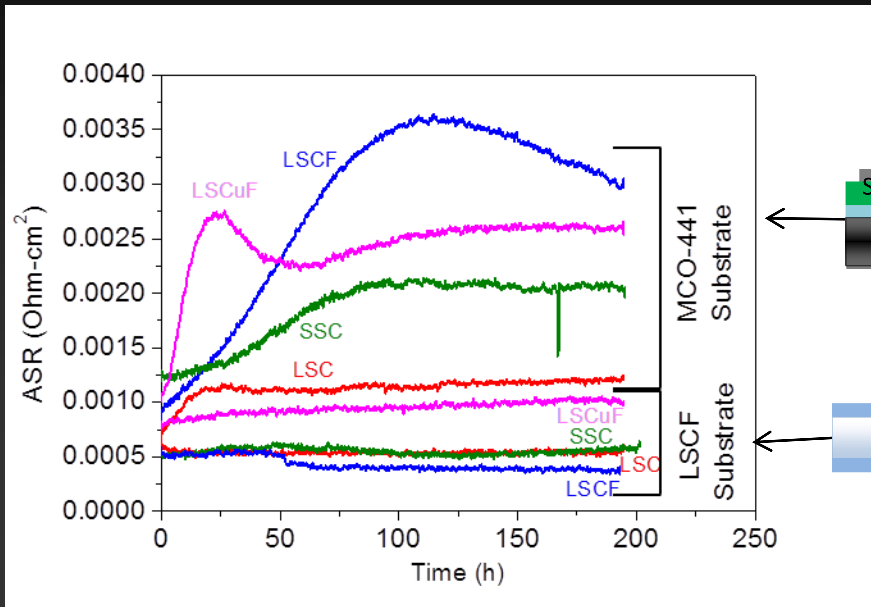
Screening Summary

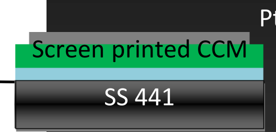
	Incipient Sintering Point (°C)	Shrinkage at 900°C	Shrinkage at 1000°C	CTE at 800°C	Reacts with MCO? 800°C 150h	Reacts with MCO? 1000°C 10h	Reacts with LSCF? 800°C 150h	Reacts with LSCF? 1000°C 10h	Conductivity of bulk dense pellet 800°C (S/cm)
LSCF	637	2.7	7.6	17.3	NO	NO	N/A	N/A	426
LSCuF	820	1.1	10.1	15.5	NO	NO	NO	NO	201
LSC	677	1.1	3.3	18.7	NO	NO	Minor	Minor	1702
SSC	740	0.5	2.3	22	NO	Trace	NO	NO	1338
SBSC	708	1.6	3.4	22	NO	Trace	YES	YES	458
GSC	760	1.3	3.2	19.5	NO	Trace	YES	YES	350
LSM	784	0.7	3.3	12.8	NO	NO	YES	YES	272
LBC	770	0.7	2.3	25	NO	NO	Minor	Minor	314
YBC	689	1.7	3.8	16.8	NO	YES	YES	YES	260
NCC	657	1.5	5.5	14.5	YES	YES	YES	YES	107
LSCMF	786	0.4	2.1	17.6	NO	NO	N/A	N/A	110
LNF	932	0	1.1	13.8	NO	NO	YES	YES	589
LSN	975	0	0.1	13.5	Minor	YES	NO	NO	352
LSF	690	0.3	0.9	13.3	NO	NO	NO	NO	133
LNC	782	0.4	2.4	14.6	NO	NO	NO	NO	11

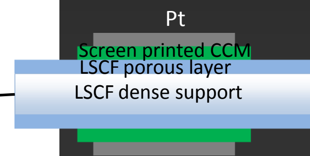
The most promising candidates are:
- LSCF: good sintering and moderate conductivity
- LSCuF: very good sintering at 1000°C
- LSC and SSC: extremely high conductivity, moderate sintering

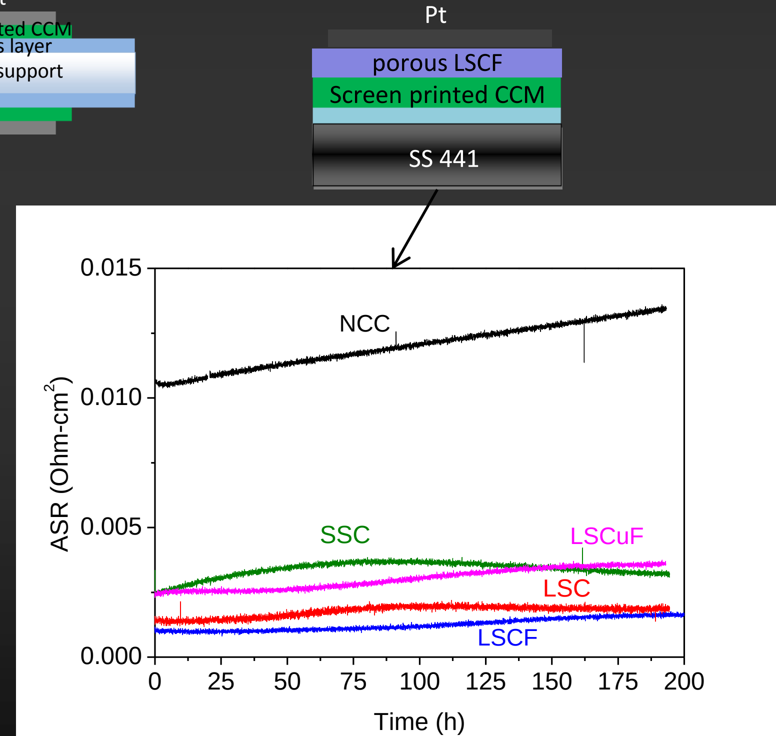
ASR Screening

800°C in air
~500mA/cm^2







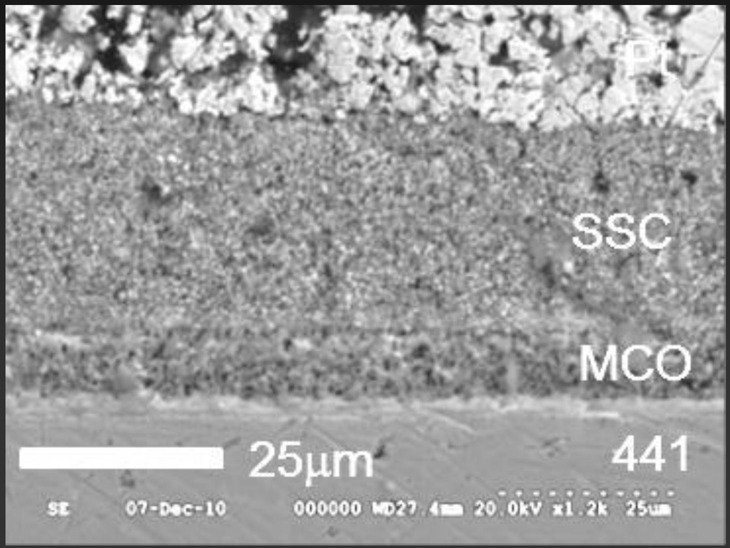


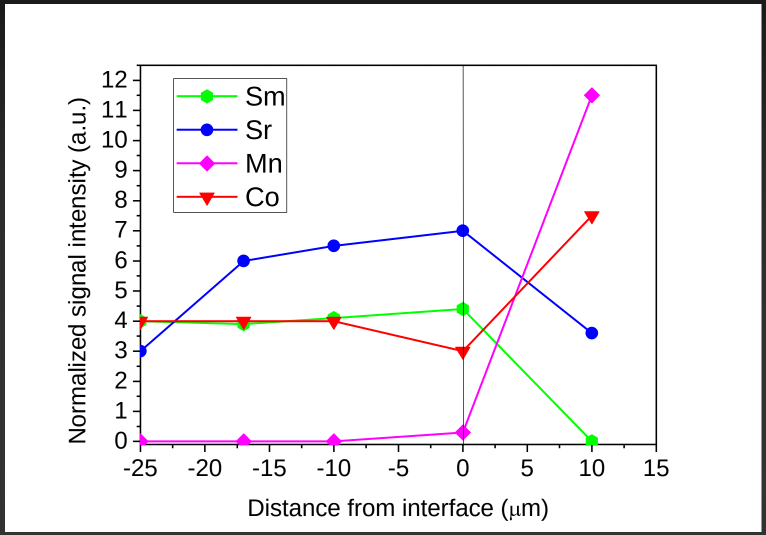
- MCO and Cr_2O_3 layers dominate ASR

- Composition of CCM may affect MCO properties and Cr_2O_3 growth rate

- NCC ASR too high and unstable
- All others acceptable

Post-Mortem Analysis of ASR Specimens

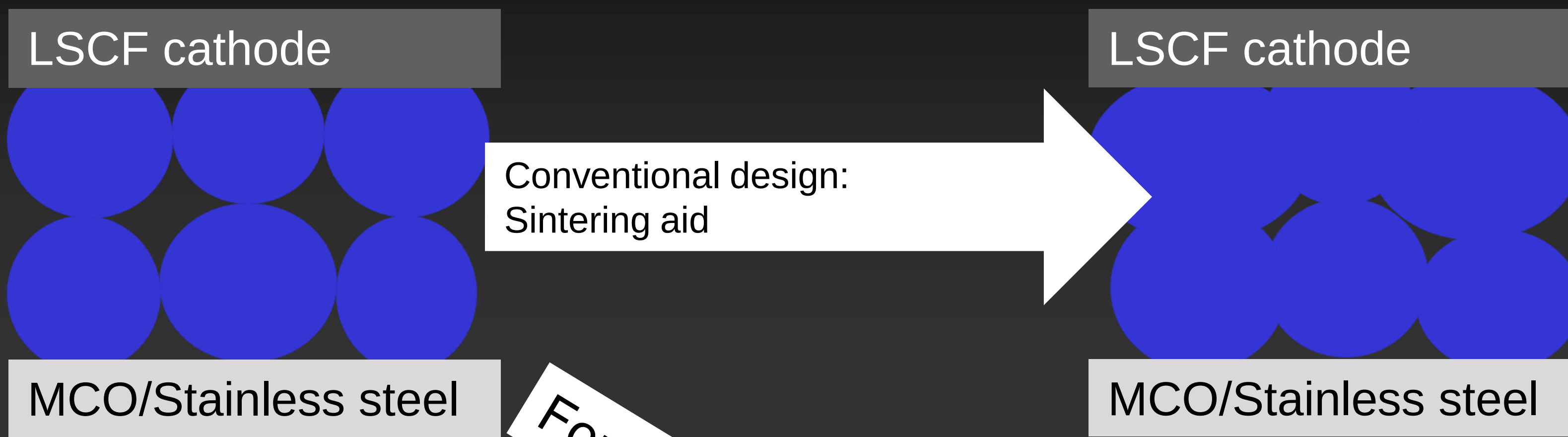


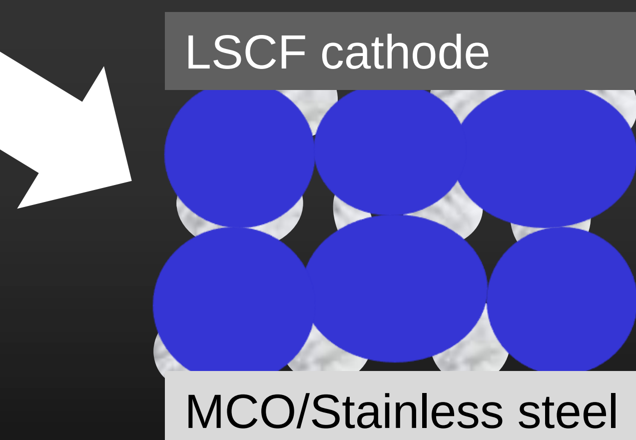


EDAX determination of interdiffusion

	CCM	LSCF	CCM	MCO
LSC	Minor Fe	none	Minor Mn	La, Sr
SSC	Minor Fe	Minor Sm	none	Sr
LSCF	N/A	N/A	none	Fe
LSCuF	none	Minor Cu	none	Minor Fe/Cu
NCC	none	none	Minor Mn	Minor Nd/Cu/Ce

Novel Composite CCM Concept

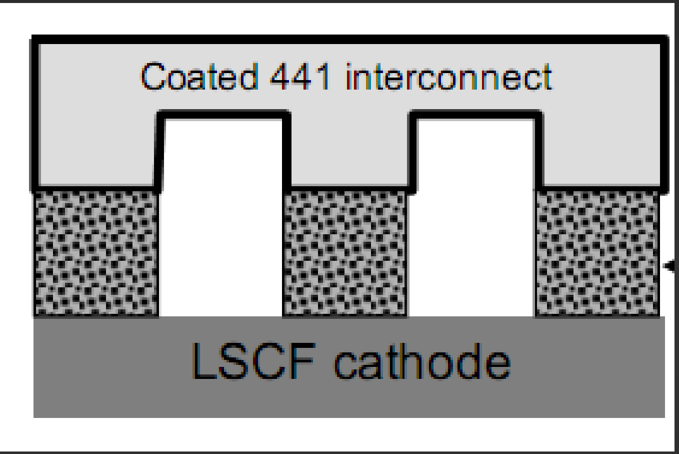




by adding
--glass
--inorganic binder

Provide bonding not only within the material but also at the interfaces

Approach 2: Glass-CCM Composites



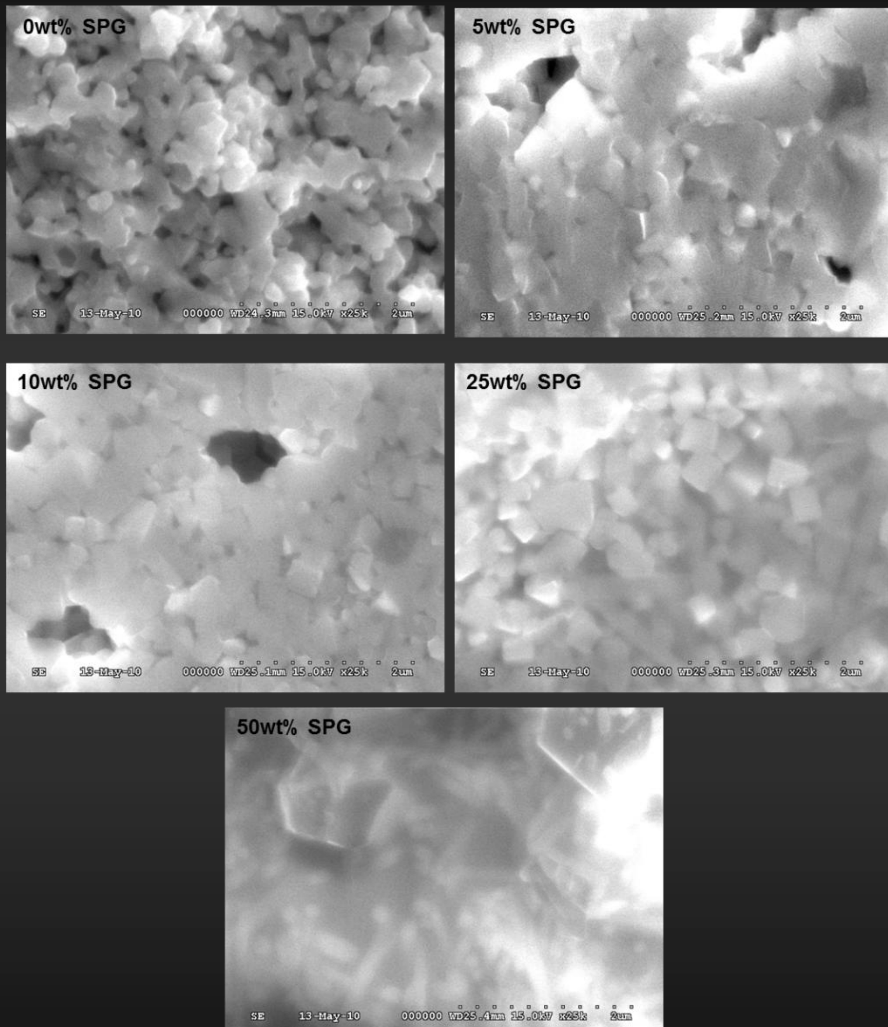
- Glasses with suitable thermal properties flow and wet the CCM, LSCF, and MCO surfaces upon 1000°C sintering

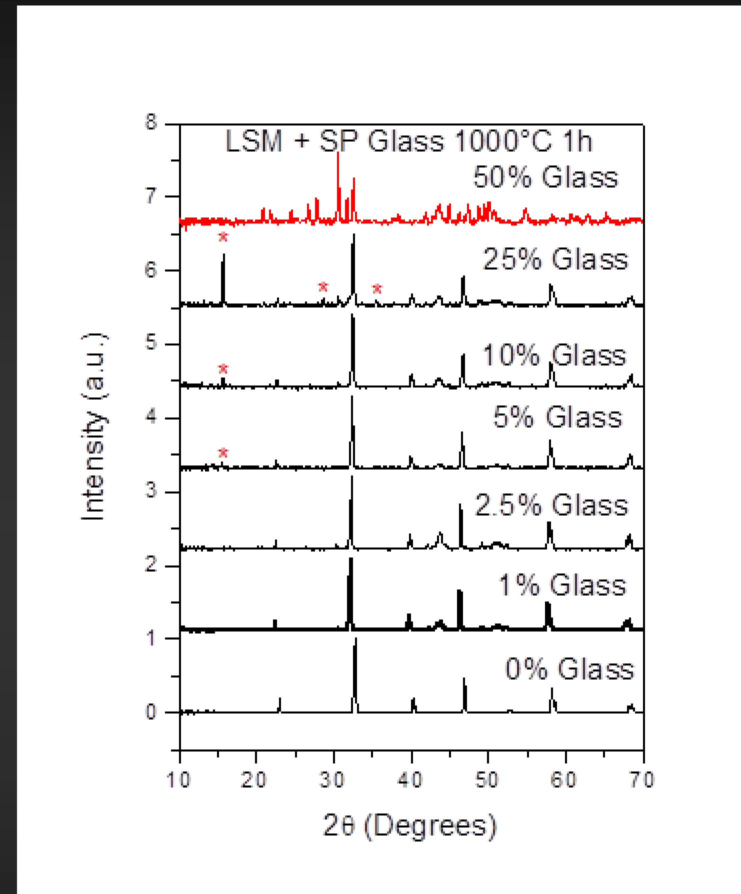
- Glass candidates chosen from the known SOFC sealing glasses

- Initial CCM candidates is LSM (high stability, good baseline)

LSM-SPG glass Composites

Spruce Pine Glass (SPG) used to assess optimal glass loading range

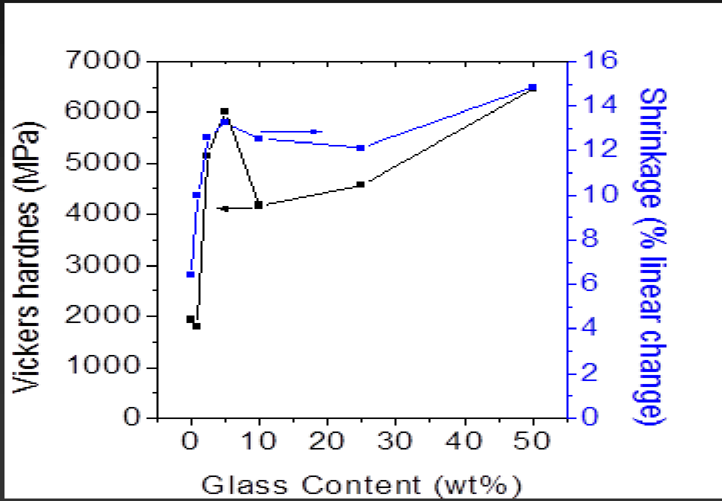




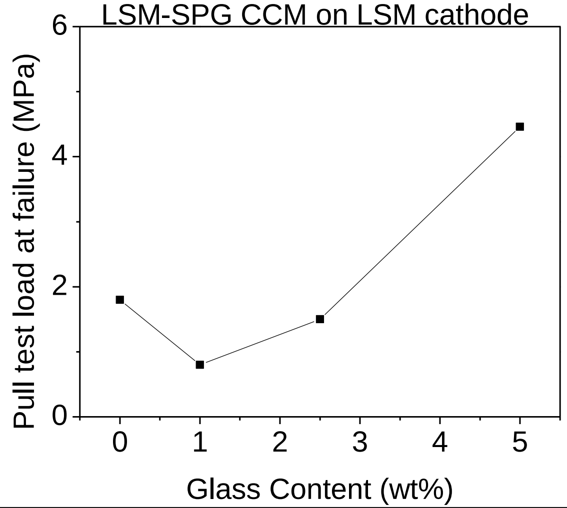
Minimal reaction at ≤10wt% glass

Significant reaction at ≥25wt% glass

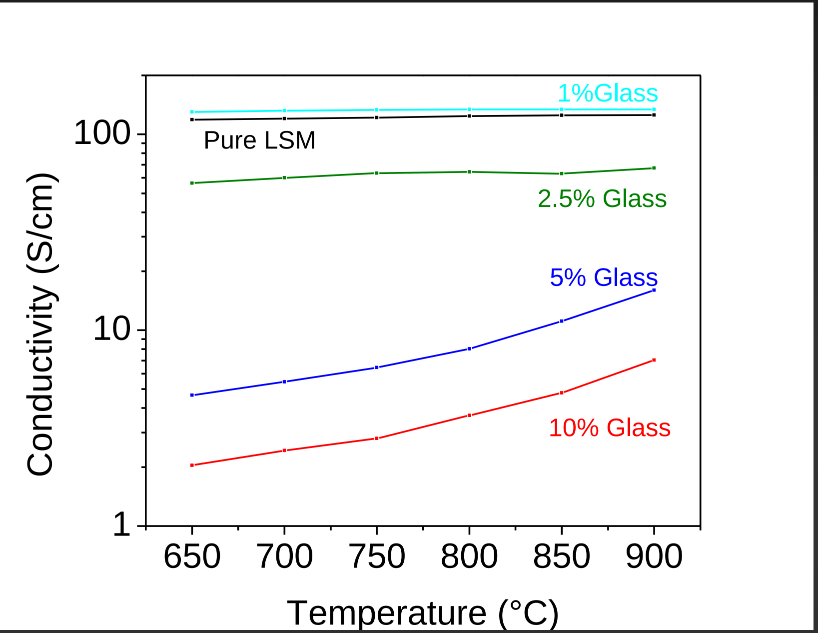
LSM-SPG glass Composites



Room-Temperature Adhesion of LSM-SPG CCM on LSM cathode



Electronic conductivity of LSM-SPG mixtures

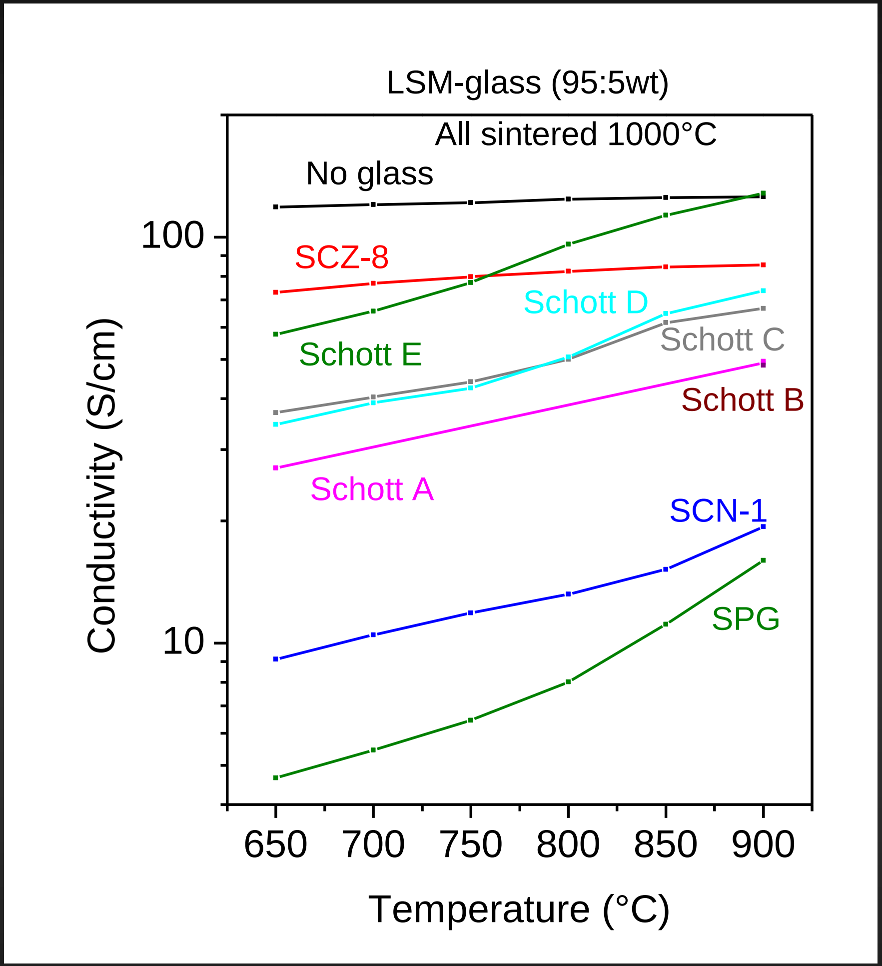


These observations suggest a trade-off between improved mechanical properties and decreased conductivity upon adding glass

→ Chose 5wt% as optimum glass loading for further work

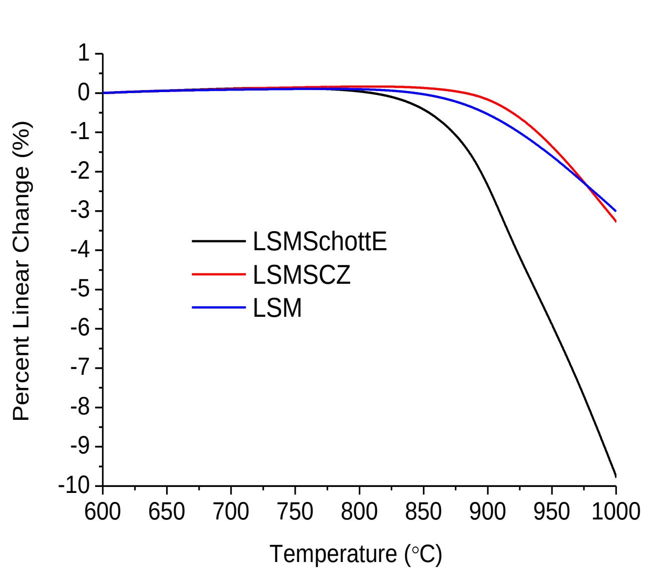
SOFC Glass-CCM Composites

Candidates:
A: Schott G018-281
B: Schott G018-305
C: Schott G018-337
D: Schott G018-311
E: Schott GM31107
SEM-COM SCN-1
SEM-COM SCZ-8



Schott E and SCZ-8 are most promising candidates – less than 50% reduction of conductivity

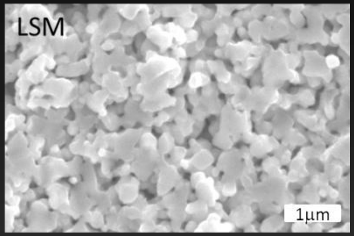
Glass-CCM Sintering Behavior

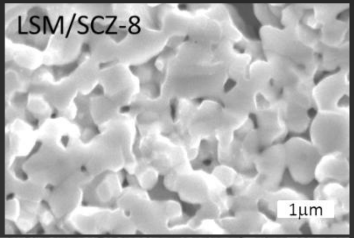


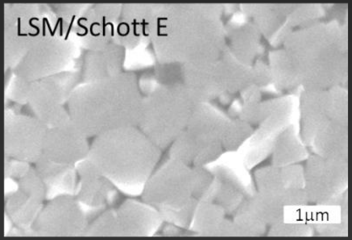
Addition of glass improves sintering at 1000°C

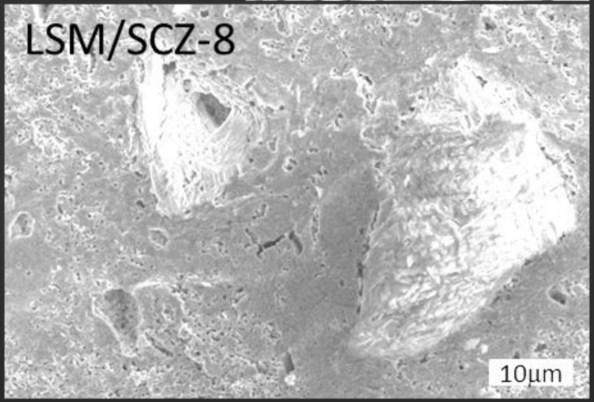
SCZ-8
- remains intact
- minimal microstructure effect

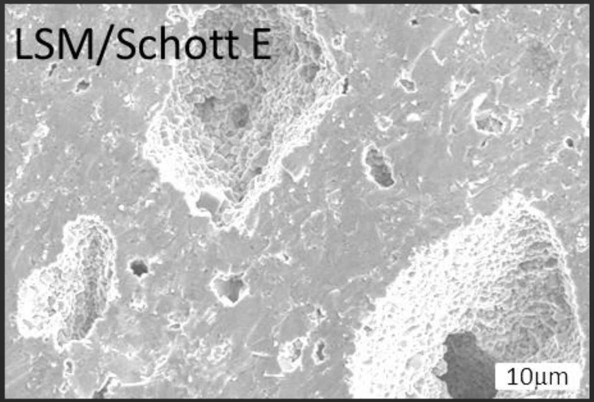
Schott E
- flows into LSM matrix
- increases grain growth









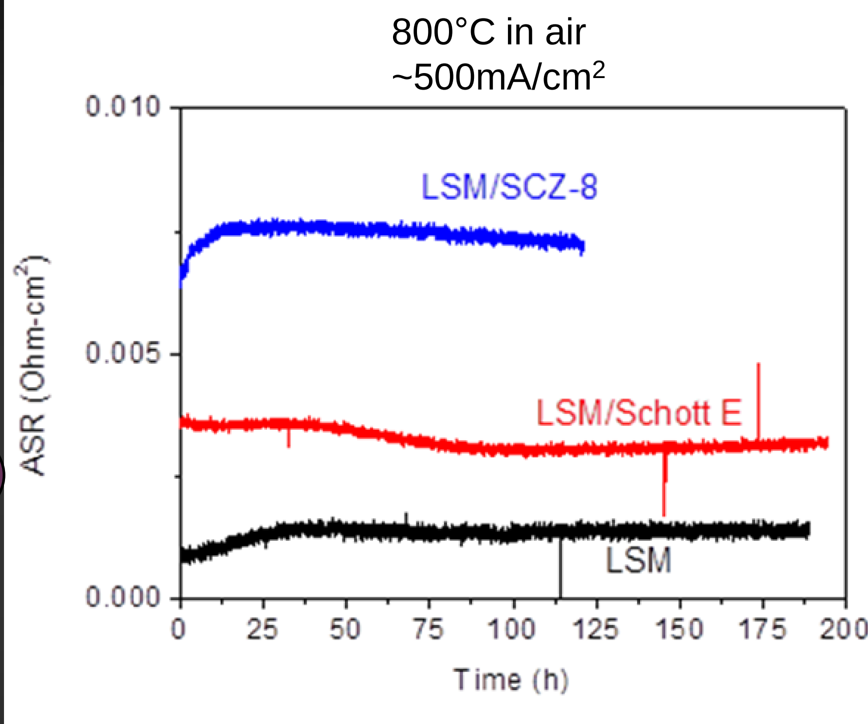


Glass identifier	CTE (10^{-6}/K)	Softening point (°C)
Schott E	10.0	649
SCZ-8	9.5	837

Mechanical Properties and ASR

1000°C Sintering
Room temperature tests

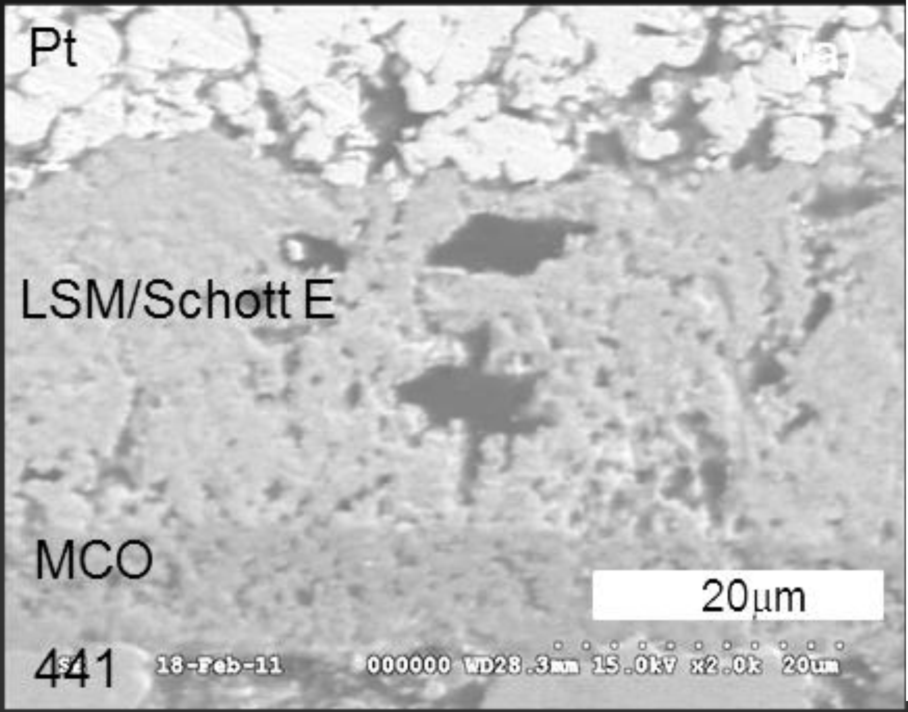
CCM	Glass	Vickers Hardness (MPa)	Adhesion on LSCF (MPa)	Adhesion on 441 MCO (MPa)
LSM	none	1931	3.9	1.8
LSM	SCZ-8	2839	**5.3**	**2.9**
LSM	Schott E	5401	**4.8**	**3.9**

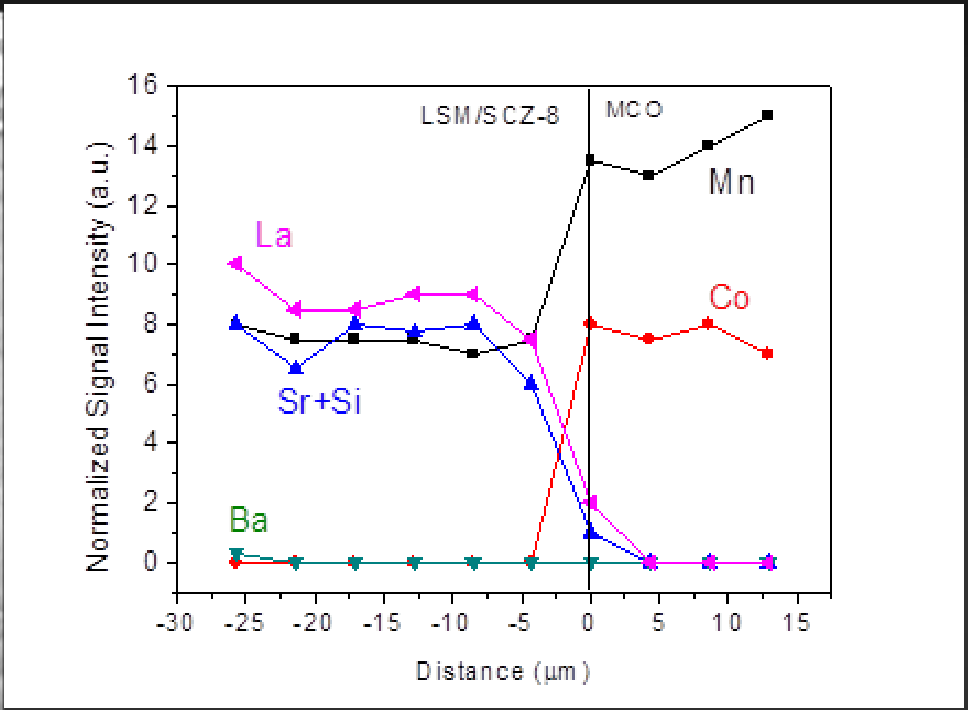


Mechanical properties improved with glass addition

Addition of glass does not significantly increase ASR of CCM/Interconnect

Post-ASR Test Analysis

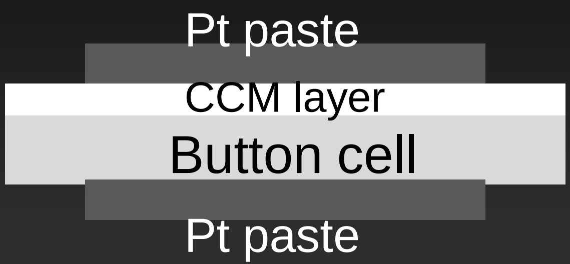




- Good interfacial adhesion

- Minimal interdiffusion between LSM/Glass and MCO

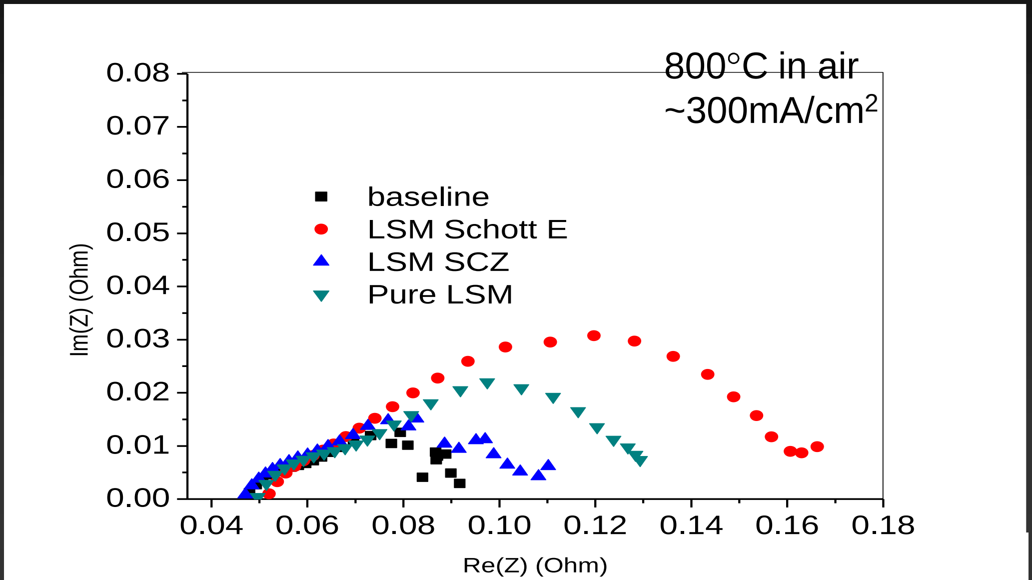
In-Situ Button Cell Stability

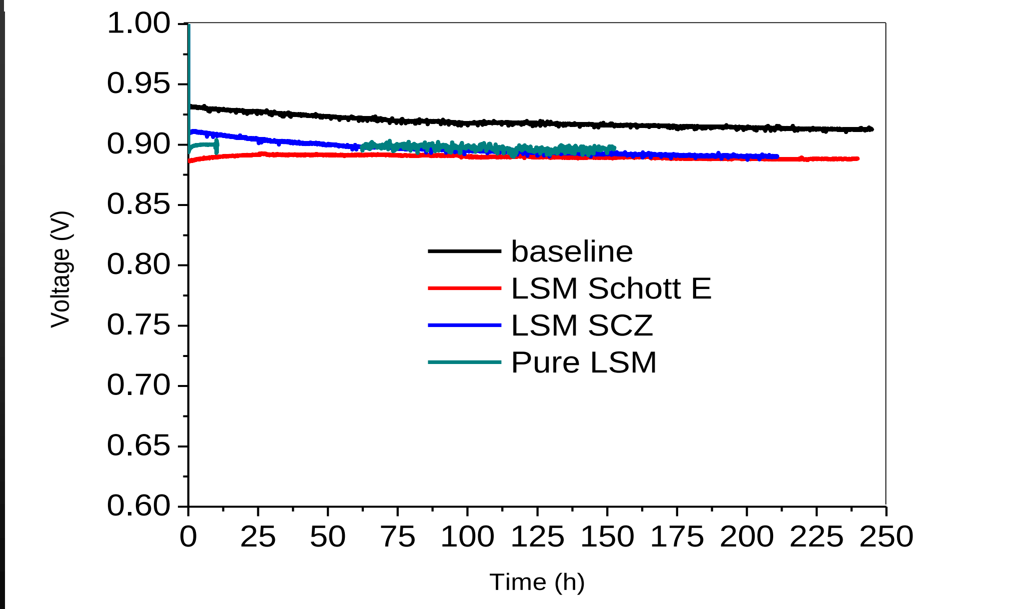


-Glass-CCM does not degrade stability of LSCF cathode

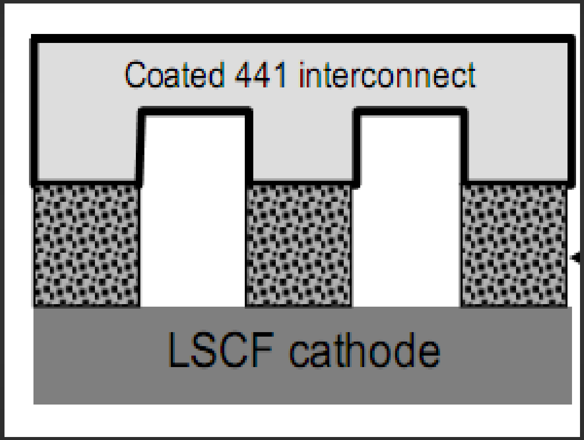
-Minimal effect on initial performance

- Upcoming tests with MCO-coated 441 interconnect will assess effect of Cr and partial current collection area





Approach 3: CCM-Inorganic Binder Composites



Add inorganic binders to improve bonding

- Aremco aqueous binders, similar to binders for 552, 516 and other well-known SOFC sealants

  Alumino-silicates, Alumino-phosphates, Silicates

Challenges:

- Reactivity between CCM and Binder?
- Binder loading optimization: improved strength vs. percolation of conductive particles

Low temperature cure, no oxidation of stainless steel in processing

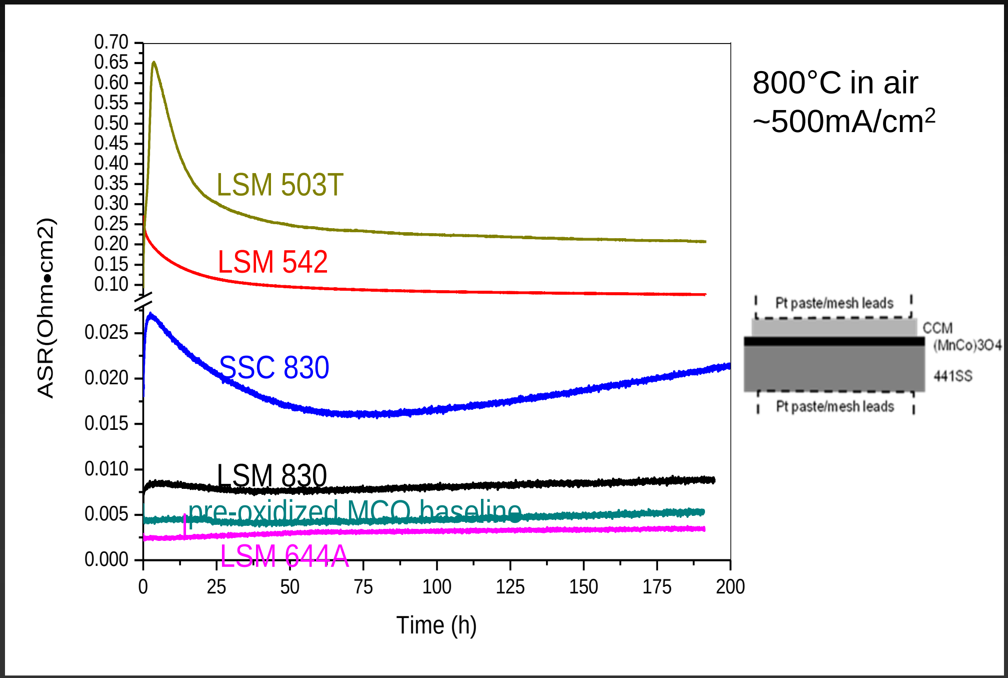
CCM-Inorganic Binder Composites Screening

Binder Type	Major Components	pH	React with LSM Powder?	React with SSC Powder?
542	Al,P, minor Si	2.5	Slight	YES
794	Al,P	3	NO	YES
795	Al,Cl	3.5	NO	Slight
644A	Al	4	NO	NO
644S	Si	9	NO	NO
830	Si, minor S	11.4	NO	NO

Acidic binders completely dissolve SSC and attack LSM

Compatible binders screened for conductivity and downselected to:
LSM-830 SSC-830
LSM-542
LSM-644A

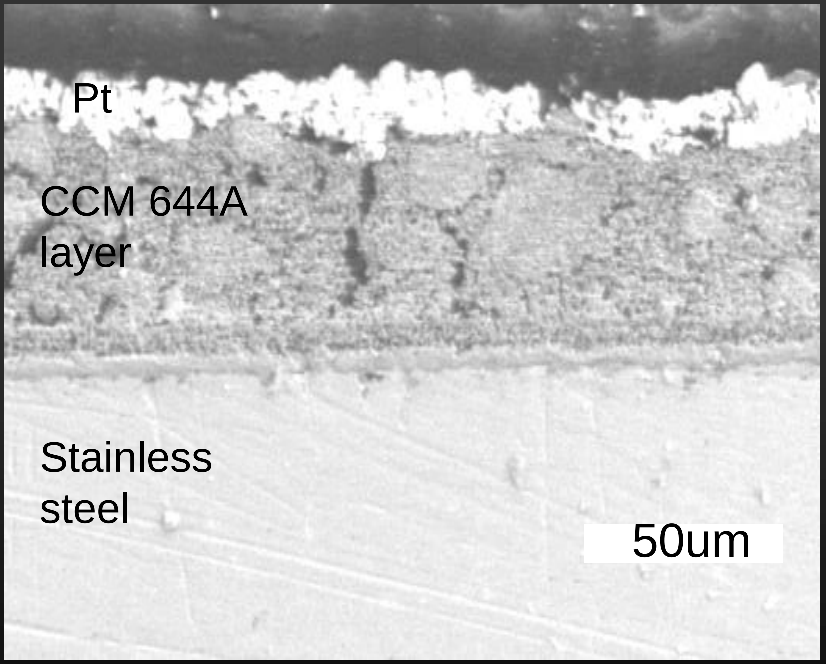
ASR of CCM-Inorganic Binder Composites



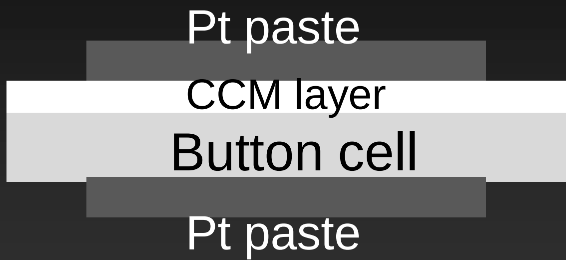
	Adhesion on MCO441 (Mpa)
LSM	1.1
LSM830	1.1
LSM644A	1.6

Room-temperature adhesion
- minimal improvement

Best candidates (LSM 644A and LSM 830) show low, stable ASR on interconnect



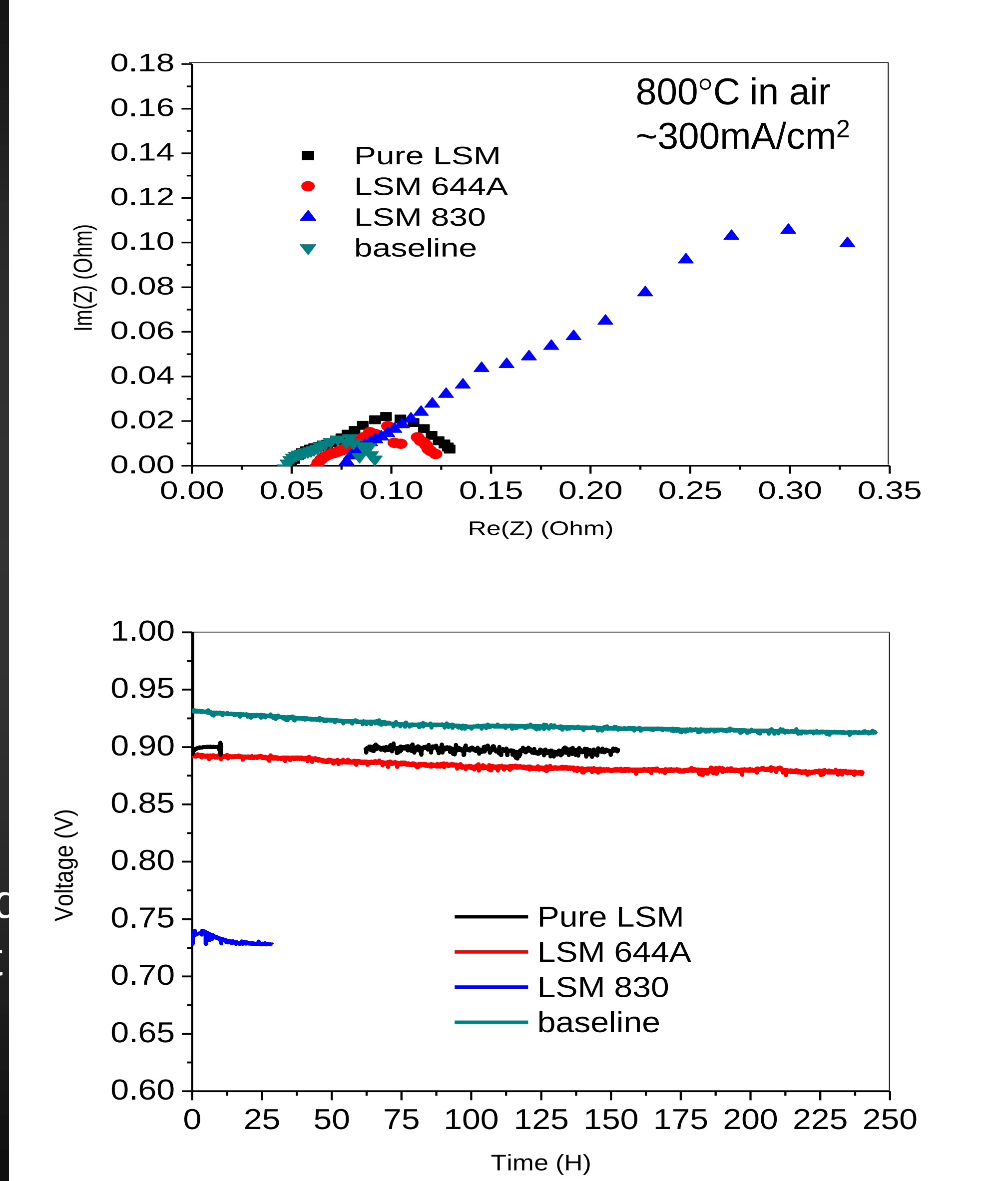
In situ Button Cell stability



-Addition of 644A does not degrade performance or stability significantly

-Addition of 830 degrades performance; suspect interaction with LSCF cathode

- Upcoming tests with MCO-coated 441 interconnect will assess effect of Cr and partial current collection area



Conclusions

Down-selected most promising conventional CCM materials

- LSCF, LSC, SSC, and LSCuF

Addition of glass improves room-temperature mechanical properties with minimal effect on electrochemical performance

- LSM/SCZ-8 better electrochemical performance
- LSM/Schott E better mechanical performance

Addition of 644A inorganic binder

- Minimal effect on electrochemical performance
- Bonding needs further improvement

Novel Composite CCM concept is promising. High temperature mechanical improvement needs to be demonstrated.

Future Directions

- In situ tests with MCO-coated 441 current collector

- Demonstrate improvement of high-temperature bonding

- Improve bonding for inorganic binder-CCM composites

- Develop composites with SSC or other high-conductivity oxide

- Composites with mixed bonding aids

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Contact Info

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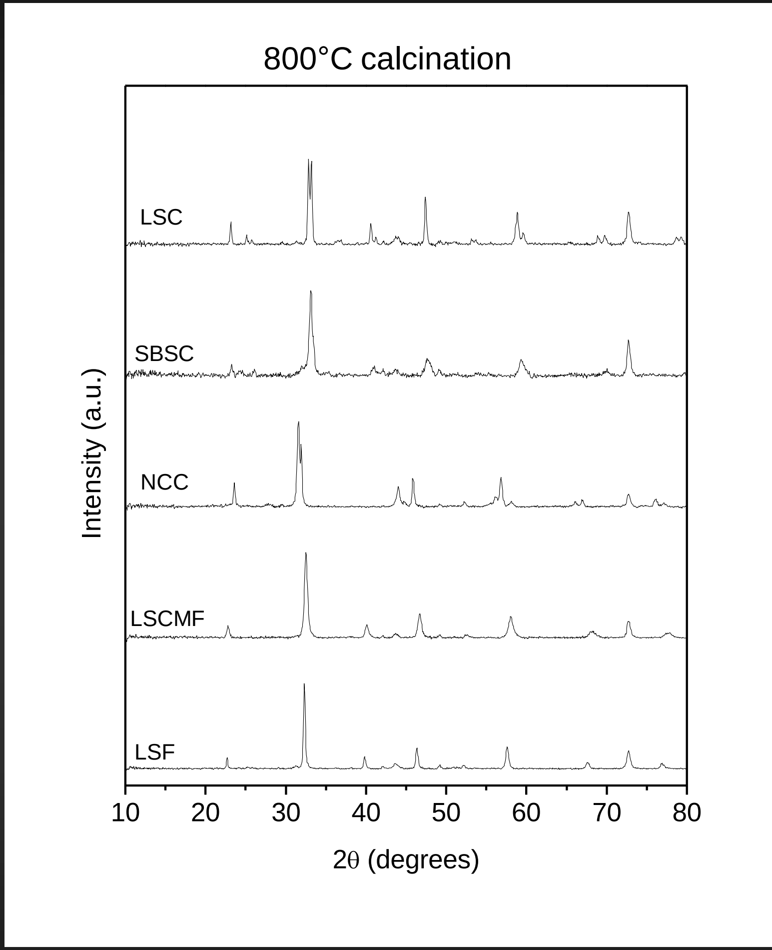
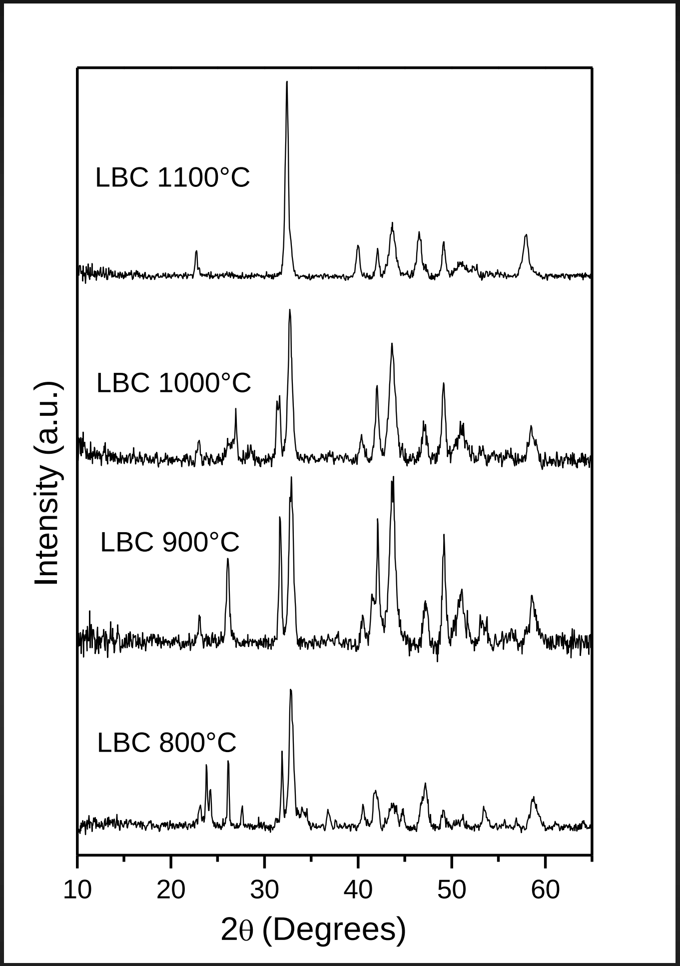
Title

Extra Slides

GNP Synthesis, Coarsening, XRD Phase Confirmation





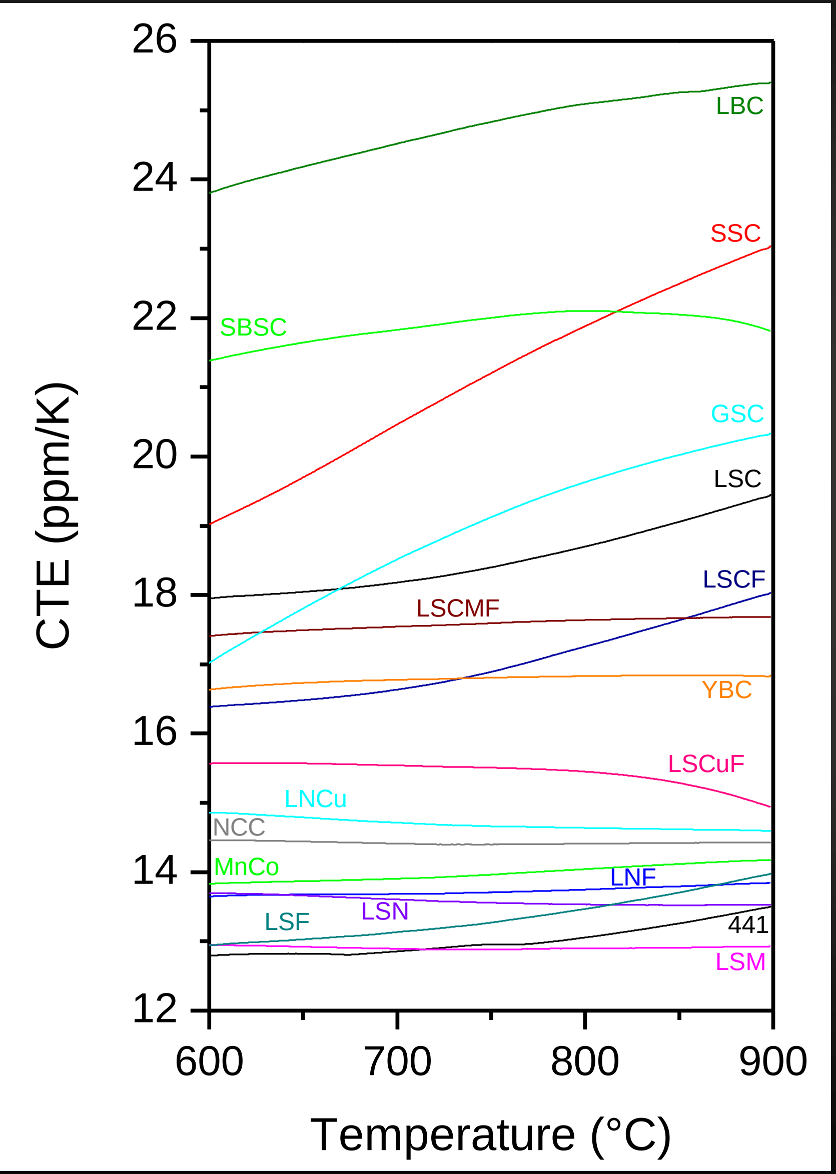
800°C: LSC, SBSC, NCC, LSCMF, LSF
900°C: GSC, LSN, LSCuF
1100°C: LBC, YBC

CTE

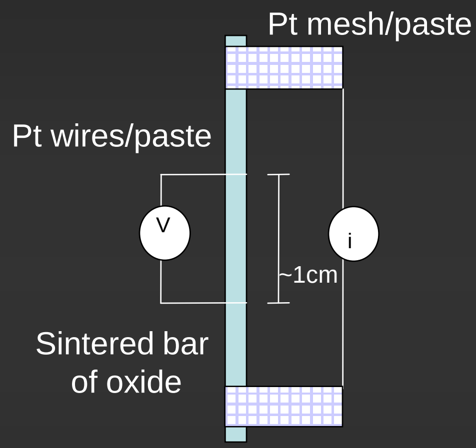
Note CTE for interconnect and cell <14ppm/K

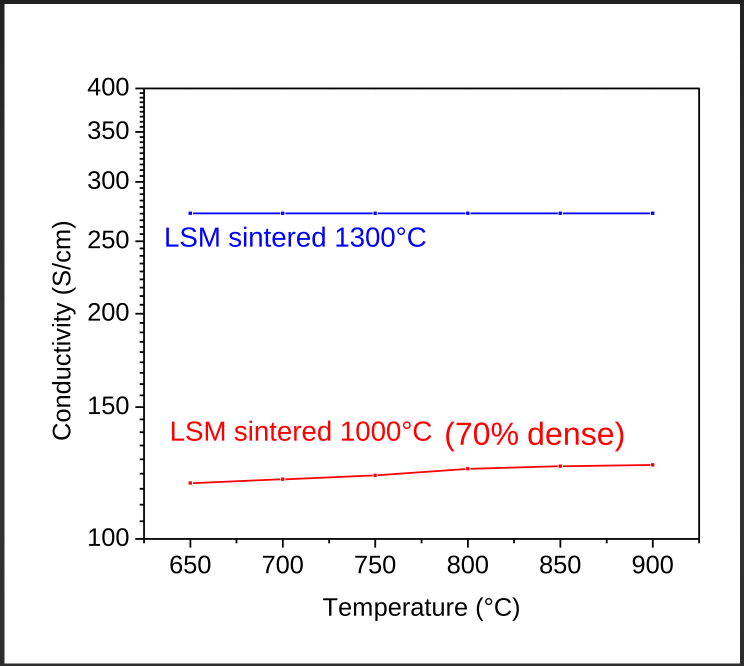
- Matched CTE is desirable

- High CTE does not disqualify candidate material
  - Thin, porous layer



Conductivity of Porous CCM



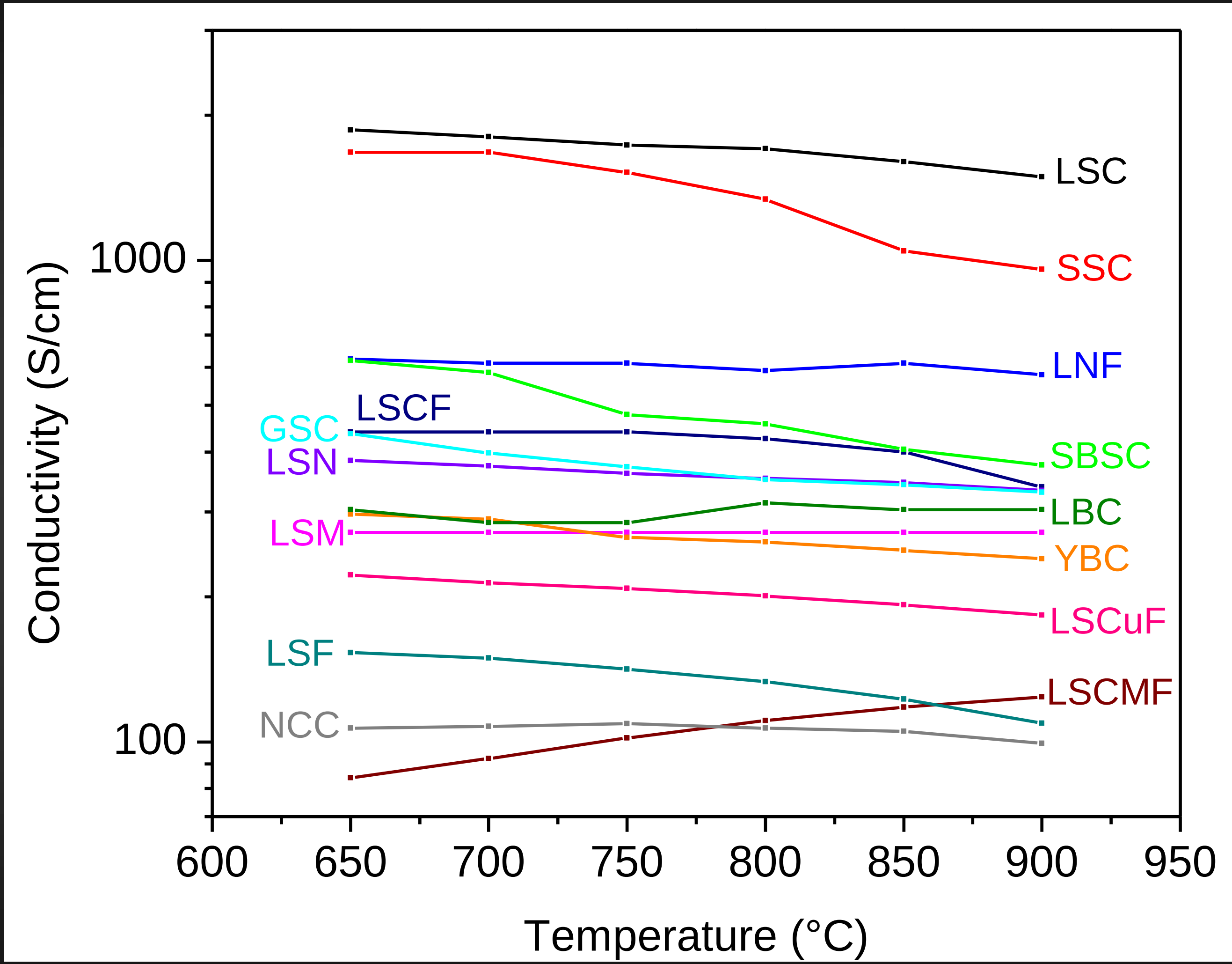


Conductivity less than predicted by density
- minimal sintering/particle necking or GB issue

Conductivity of Dense CCM

- Measured for dense bars

- Conductivity of porous CCM after bonding at 900-1000°C will be lower

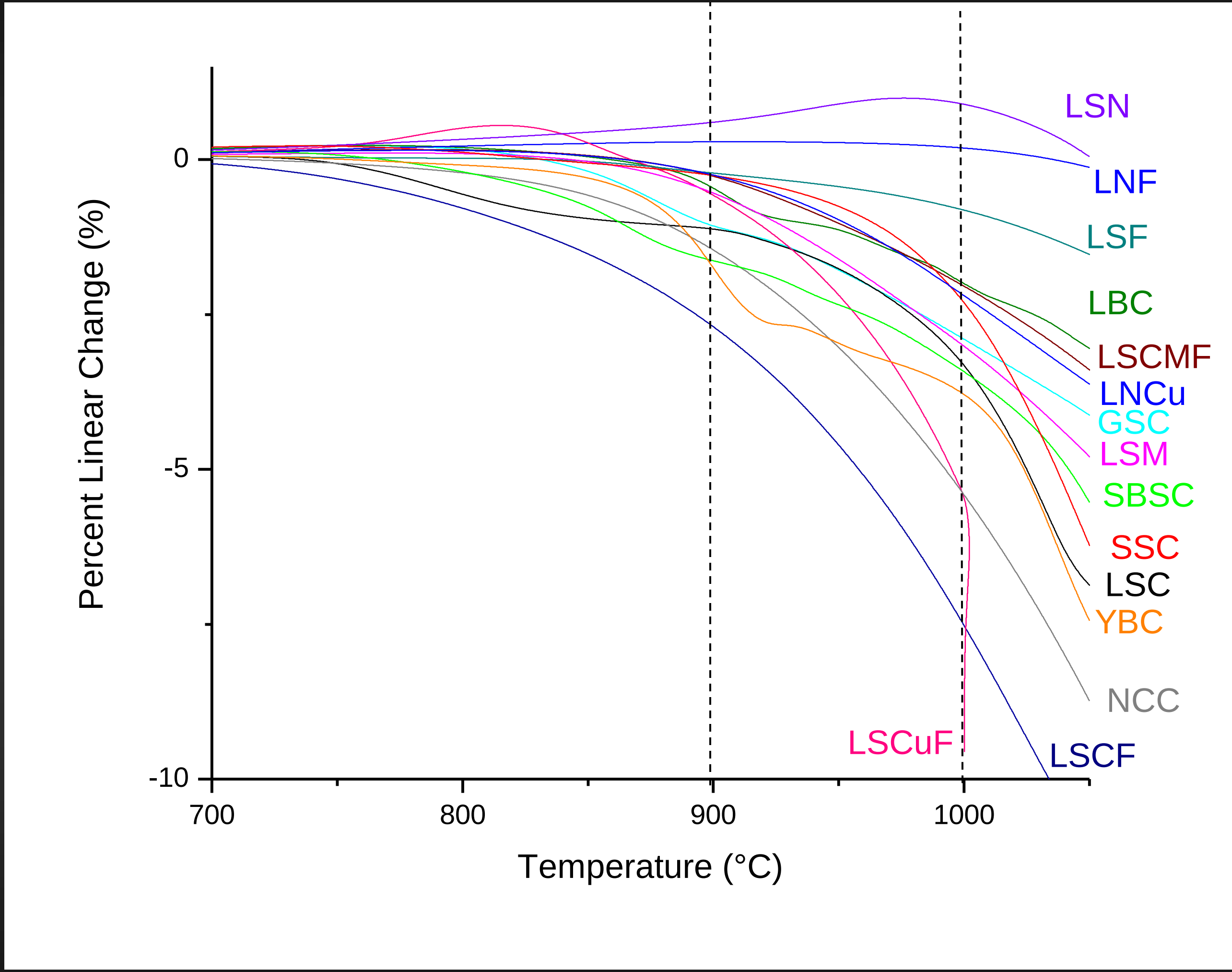


Sintering Behavior

- Extent-of-sintering related to strength in the CCM layer

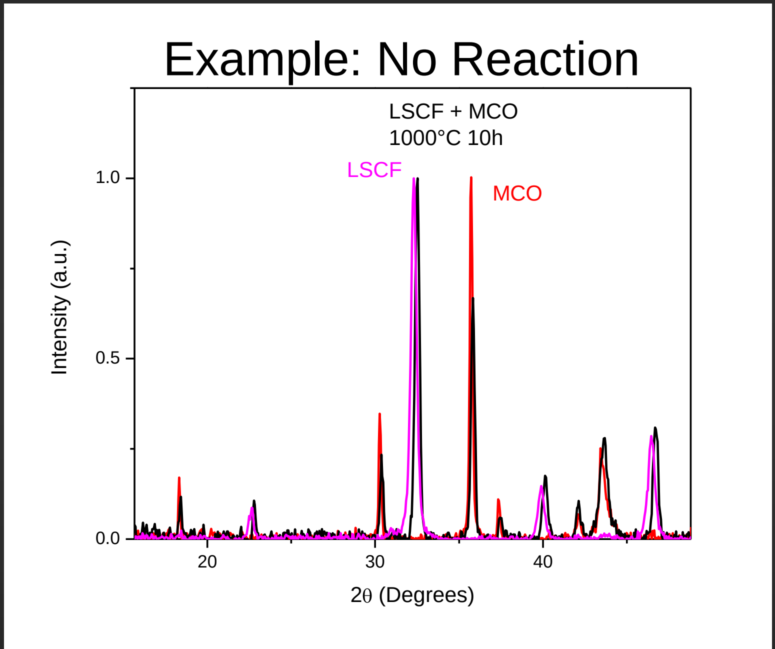
(not necessarily related to bonding at the interface with neighbor layers)

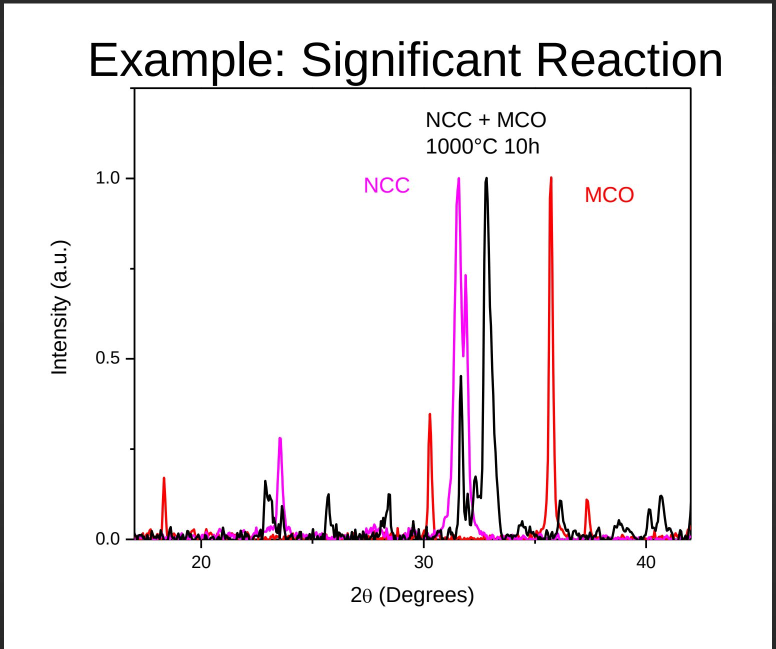
- Only a few candidates display significant sintering in the 900-1000°C range



Reactivity with Neighbor Materials

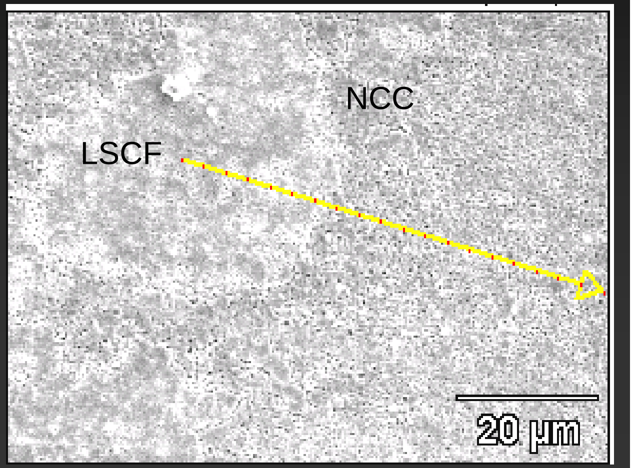
Pellets of mixed MCO/CCM and LSCF/CCM
Reacted in air at: Operating conditions (800°C 120h) and Sintering conditions (1000°C 10h)

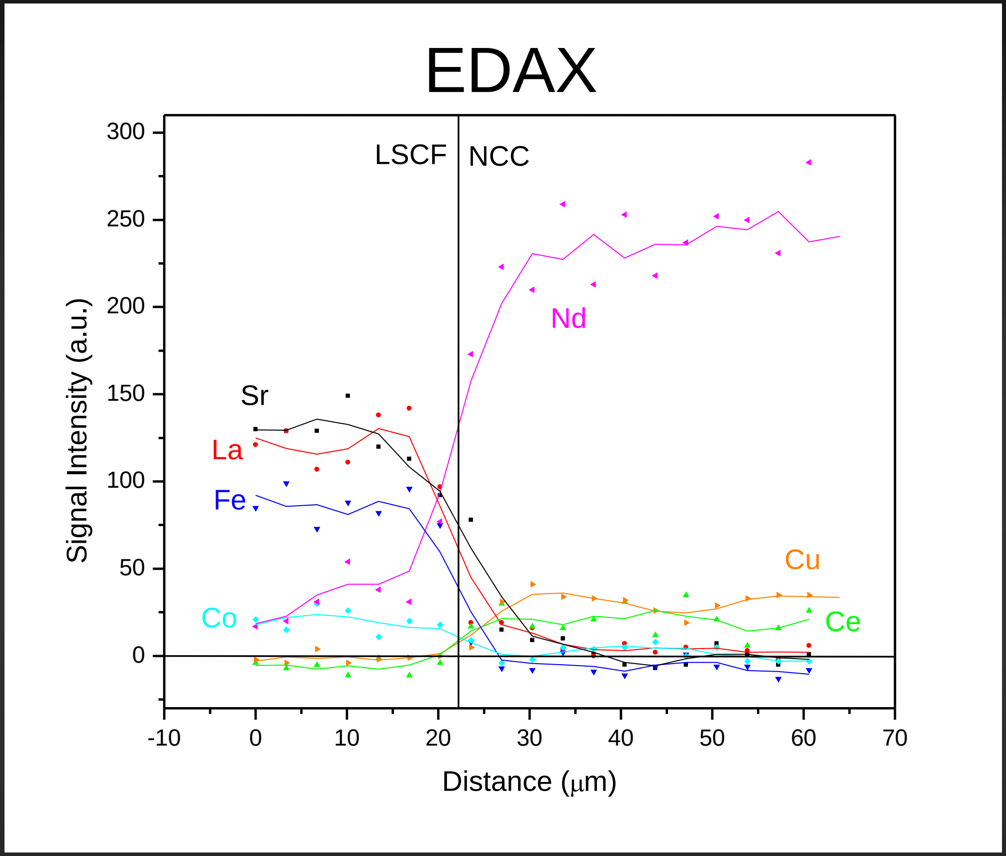




Most candidates were non-reactive with MCO, but reacted with LSCF

Reaction/Diffusion Distance





In all cases, reaction zone restricted to <40μm

→ reaction may be acceptable for

- thick LSCF layer
- electrically conductive reaction products